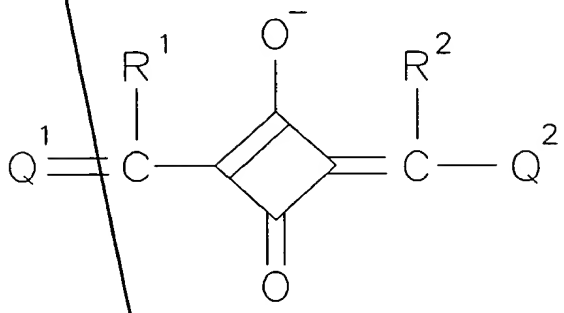
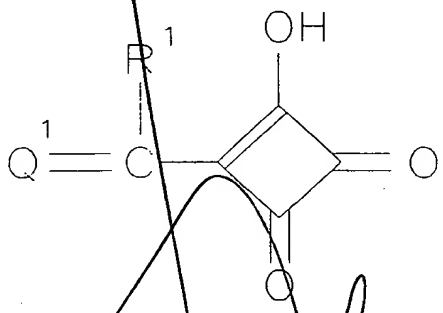
CLAIMS

1. A process for the preparation of a squarylium compound of the formula:



wherein Q^1 and Q^2 are each independently an aromatic heterocyclic nucleus such that in the compounds of formulae $Q^1CH_2R^1$ and $Q^2CH_2R^2$ the methylene hydrogens are active hydrogens, and R^1 and R^2 are each independently a hydrogen atom or an aliphatic or cycloaliphatic group,

which process comprises reacting a squaric acid derivative of the formula:



wherein Q^1 and R^1 are as defined above, with a compound of the formula $Q^2CH_2R^2$.

2. A process according to claim 1 which is carried out in the presence of a base or a Lewis acid.

3. A process according to claim 1 wherein the atoms of Q^1 and Q^2 which are bonded directly to the CR^1 and CR^2 groupings respectively are each part of an aromatic ring.

4. A process according to claim 3 wherein at least one of Q^1 and Q^2 is a pyrylium, thiopyrylium, selenopyrylium, benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus.

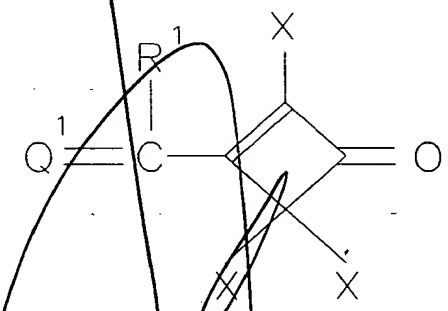
5. A process according to claim 4 wherein each of Q^1 and Q^2 is a pyrylium, thiopyrylium, selenopyrylium, benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus.

6. A process according to claim 5 wherein each of Q^1 and Q^2 is a 4-pyrylium, 4-thiopyrylium, 4-selenopyrylium, 4-benzpyrylium, 4-benzthiopyrylium or 4-benzselenopyrylium nucleus.

7. A process according to claim 1 wherein Q^1 and Q^2 are different.

8. A process according to claim 7 wherein one of Q^1 and Q^2 is a 2-(o-alkoxyphenyl) benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus, and the other is a 2-alkyl, 2-alkenyl, 2-alkynyl or 2-alicyclic benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus, or a 2, 6-di(alkyl or cycloalkyl) pyrylium, thiopyrylium or selenopyrylium nucleus.

9. A process according to claim 1 wherein the squaric acid derivative has been prepared by hydrolysis of a trihalosquaric acid derivative of the formula:



wherein Q^1 is an aromatic heterocyclic nucleus such that in the compound of formula $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens, and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, and X represents chlorine or bromine.

10. A process according to claim 9 wherein, in the trihalosquaric acid derivative, X represents chlorine.

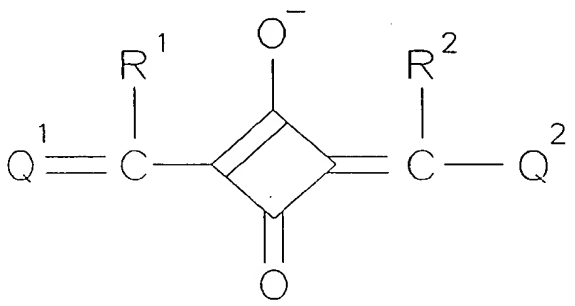
11. A process according to claim 9 wherein the hydrolysis is effected using triflic acid and water.

12. A process according to claim 9 wherein the trihalosquaric acid derivative has been prepared by reaction of a compound of the formula $Q^1CH_2R^1$ and a 1,2,4,4-tetrahalocyclobut-1-en-3-one in the presence of a base.

13. A process according to claim 12 wherein the reaction is conducted by contacting the two reactants with a basic resin.

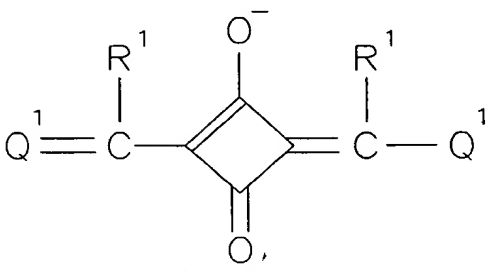
14. A process according to claim 1 wherein the squaric acid derivative has been prepared by reacting a diester, monoacid chloride monoester or diacid chloride of squaric acid with a compound of the formula $Q^1CH_2R^1$, followed by hydrolysis of the resultant monoacid chloride or monoester intermediate.

15. A squarylium compound of the formula:

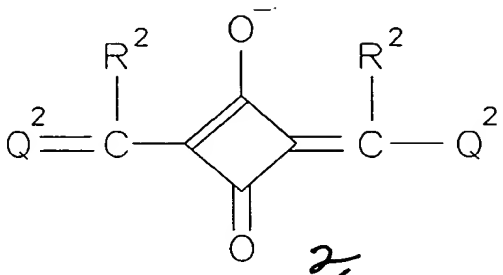


wherein Q^1 and Q^2 are each independently a pyrylium, thiopyrylium, selenopyrylium, benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus, and R^1 and R^2 are each independently a hydrogen atom or an aliphatic or cycloaliphatic group, the Q^1CR^1 grouping being different from the Q^2CR^2 grouping.

16. A squarylium compound according to claim 15 which is essentially free from squarylium compounds of the formulae:



and



17. A squarylium compound according to claim 16 wherein each of Q^1 and Q^2 is a 4-pyrylium, 4-thiopyrylium, 4-selenopyrylium, 4-benzpyrylium, 4-benzthiopyrylium or 4-benzselenopyrylium nucleus.

18. A squarylium compound according to claim 17 wherein at least one of Q^1 and Q^2 is a 2,6-dialkylpyrylium, -thiopyrylium or -selenopyrylium nucleus, in which each of the alkyl groups contains not more than about 8 carbon atoms.

19. A squarylium compound according to claim 18 wherein at least one of Q^1 and Q^2 is a 2,6-di-tertiary butylpyrylium, -thiopyrylium or -selenopyrylium nucleus.

20. A squarylium compound according to claim 17 wherein one of Q^1 and Q^2 is a 2-phenyl benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus and the other is (a) a 2-substituted benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus, in which the 2-substituent is an alkyl, alkenyl, alkynyl or alkicyclic group, or (b) a 2,6-dialkyl ~~butyl~~pyrylium, -thiopyrylium or -selenopyrylium nucleus.

21. A squarylium compound according to claim 20 wherein the 2-phenyl group has an *ortho* alkoxy or cycloalkoxy substituent.

22. A squarylium compound according to claim 17 wherein one of Q^1 and Q^2 is a benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus bearing at its 7-position an ~~an~~ $-N[(CH_2)_3-]_2$ grouping in which the ends of the trimethylene groups remote from the nitrogen atom are joined to the 6- and

8-positions of the nucleus, so that the $-N[-(CH_2)_3-]_2$ grouping and the phenyl ring of the nucleus together form a julolidine ring system, and the other is (a) a 2-substituted benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus, in which the 2-substituent is an alkyl, alkenyl, alkynyl or alicyclic group, or (b) a 2,6-dialkyl-~~butyl~~pyrylium, -thiopyrylium or -selenopyrylium nucleus.

23. A squarylium compound according to claim 17 wherein at least one of Q^1 and Q^2 is a benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus bearing at its 6-position an alkoxy or cycloalkoxy group.

24. A squarylium compound according to claim 15 in which:

(a) Q^1 is a 2,6-bis(1,1-dimethylethyl)-4-pyrylidene grouping, Q^2 is a 2,6-bis(1,1-dimethylethyl)-4-thiopyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely [4-[[3-2,6-bis(1,1-dimethylethyl)-(4H-pyran-4-ylidene)-methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)thiopyrylium hydroxide inner salt;

(b) Q^1 is a 2,6-bis(1,1-dimethylethyl)-4-pyrylidene grouping, Q^2 is a 2,6-bis(1,1-dimethylethyl)-4-selenopyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely [4-[[3-2,6-bis(1,1-dimethylethyl)-(4H-pyran-4-ylidene)-methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)-selenopyrylium hydroxide inner salt;

(c) Q^1 is a 7-diethylamino-2-(1,1-dimethylethyl)benz[b]-4H-pyran-4-ylidene grouping, Q^2 is a 7-diethylamino-2-phenylbenzpyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely 4-[3-[[7-diethylamino-2-(1,1-dimethylethyl)benz[b]-4H-pyran-4-ylidene]methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-7-diethylamino-2-phenylbenzpyrylium hydroxide inner salt dye;

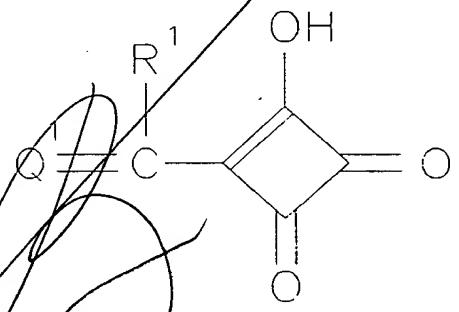
(d) Q^1 is a 2,6-bis[1,1-dimethylethyl]-4-selenopyrylidene grouping, Q^2 is a 2-[2-trifluoromethylphenyl]benz[b]pyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely 4-[[3-[2,6-bis[1,1-dimethylethyl]-[4H-selenopyran-

4-ylidene]methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-2-[2-trifluoromethylphenyl]benz[b]pyrylium hydroxide inner salt dye;

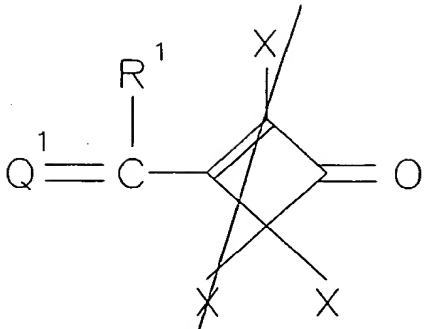
(e) Q^1 is a 6-[but-2-oxy]-2-[1,1-dimethylethyl]benz[b]-4H-pyran-4-ylidene grouping, Q^2 is a 6-[2-ethylbut-1-oxy]-2-phenylbenzpyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely 4-[[3-[[6-[but-2-oxy]-2-[1,1-dimethylethyl]benz[b]-4H-pyran-4-ylidene]methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-6-[2-ethylbut-1-oxy]-2-phenylbenzpyrylium hydroxide inner salt dye; and

(f) Q^1 is a 2,6-bis[1,1-dimethylethyl]-4-thiopyrylidene grouping, Q^2 is a 2,6-bis[2,4-dimethylphenyl]pyrylium grouping, and R^1 and R^2 are each a hydrogen atom, namely 4-[[3-[2,6-bis[1,1-dimethylethyl]-[4H-thiopyran-4-ylidene]-methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-2,6-bis[2,4-dimethylphenyl]-pyrylium hydroxide inner salt dye.

25. A process for the preparation of a squaric acid derivative of the formula:



wherein Q^1 is an aromatic heterocyclic nucleus such that in the compound of formula $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens, and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, which process comprises hydrolyzing a trihalosquaric acid derivative of the formula:

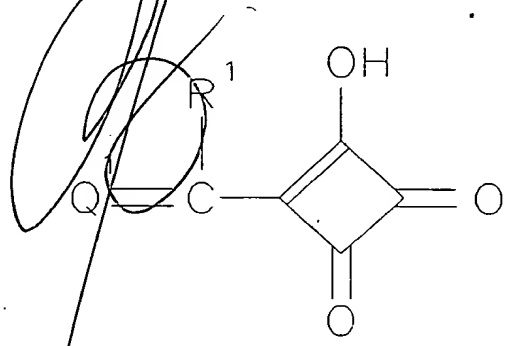


wherein Q^1 and R^1 are as defined above, and X represents chlorine or bromine.

26. A process according to claim 25 wherein, in the trihalosquaric acid derivative, X represents chlorine.

27. A process according to claim 25 wherein the hydrolysis is effected using triflic acid in water.

28. A process for the preparation of a squaric acid derivative of the formula:

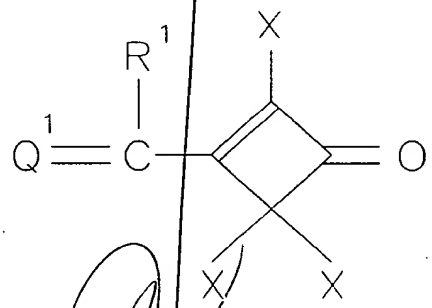


wherein Q^1 is an aromatic heterocyclic nucleus such that in the compound of formula $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens, subject to the proviso that in Q^1 a carbon atom is bonded to the carbon atom carrying the group R^1, and said carbon atom is not bonded directly to a nitrogen atom, and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, which process comprises reacting a diester, monoacid chloride monoester or diacid chloride of squaric acid with a compound of the formula $Q^1CH_2R^1$, followed by hydrolysis of the resultant monoacid chloride or monoester intermediate.

29. A process according to claim 28 wherein Q^1 is a non-nitrogenous heterocyclic nucleus.

30. A process according to claim 29 wherein Q^1 is a pyrylium, thiopyrylium, selenopyrylium, benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus.

31. A process for the preparation of a trihalosquaric acid derivative of the formula:

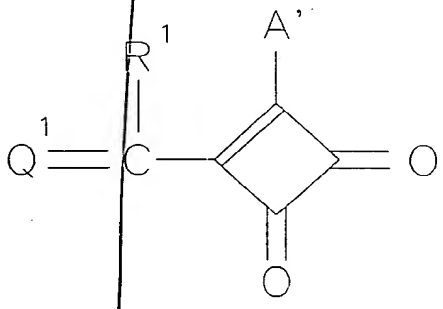


wherein Q^1 is an aromatic heterocyclic nucleus such that in the compound of formula $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens, and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, and X represents chlorine or bromine, which process comprises condensing a 2,3,4,4-tetrahalocyclobut-2-en-1-one with a compound of the formula $Q^1CH_2R^1$ in the presence of a base.

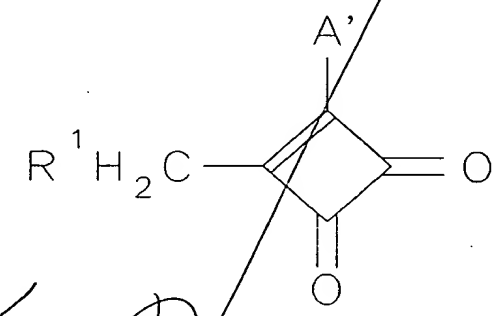
32. A process according to claim 31 wherein the base comprises a basic resin or a tertiary amine.

33. A process according to claim 31 wherein the 2,3,4,4-tetrahalocyclobut-2-en-1-one is 2,3,4,4-tetrachlorocyclobut-2-en-1-one.

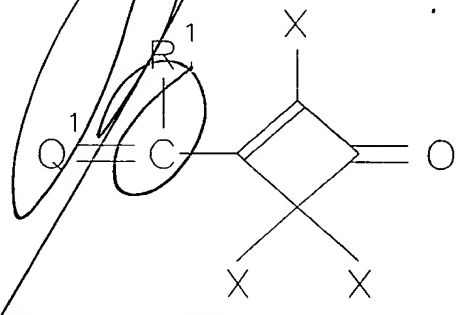
34. A process for the preparation of a squaric acid derivative of the formula:



wherein Q^1 is a 4-pyrylium, 4-thiopyrylium, 4-selenopyrylium, 4-benzpyrylium, 4-benzthiopyrylium or 4-benzselenopyrylium nucleus, R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, and A' is an esterified hydroxyl group, which process comprises reacting a chromone of the formula Q^1=O with a squaric acid derivative of the formula:



35. A squaric acid derivative of the formula:



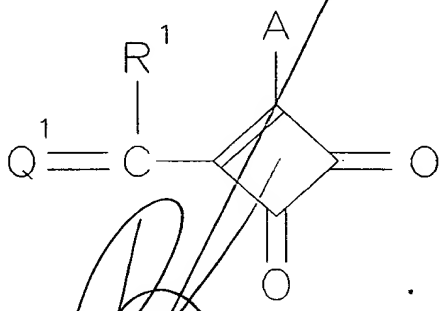
wherein Q^1 is an aromatic heterocyclic nucleus such that in the compounds of formulae $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group; and each X is a chlorine or bromine atom.

36. A squaric acid derivative according to claim 35 wherein Q^1 is a 2-(o-alkoxyphenyl) benzpyrylium, benzthiopyrylium or benzselenopyrylium group.

37. A squaric acid derivative according to claim 35 wherein Q^1 is a 6-alkoxy or 6-cycloalkoxy benzpyrylium, benzthiopyrylium or benzselenopyrylium group.

38. A squaric acid derivative according to claim 35 wherein Q^1 is a benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus bearing at its 7-position an $-N[(CH_2)_3-]_2$ grouping in which the ends of the trimethylene groups remote from the nitrogen atom are joined to the 6- and 8-positions of the nucleus, so that the $-N[-(CH_2)_3-]_2$ grouping and the benzene ring of the nucleus together form a julolidine ring system.

39. A squaric acid derivative of the formula:



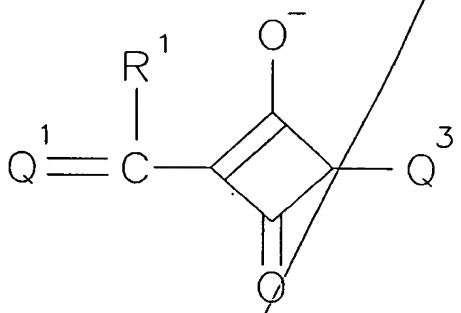
wherein Q^1 is a heterocyclic nucleus such that in the compounds of formulae $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens and R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group; and A is a chlorine or bromine atom, a hydroxyl group or an esterified hydroxyl group.

40. A squaric acid derivative according to claim 39 wherein Q^1 is a 2-(o-alkoxyphenyl) benzpyrylium, benzthiopyrylium or benzselenopyrylium group.

41. A squaric acid derivative according to claim 39 wherein Q^1 is a 6-alkoxy or 6-cycloalkoxy benzpyrylium, benzthiopyrylium or benzselenopyrylium group.

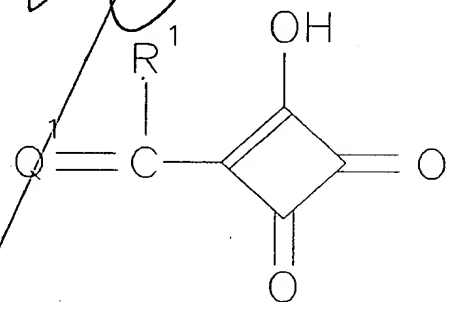
42. A squaric acid derivative according to claim 39 wherein Q^1 is a benzpyrylium, benzthiopyrylium or benzselenopyrylium nucleus bearing at its 7-position an $-N[(CH_2)_3-]_2$ grouping in which the ends of the trimethylene groups remote from the nitrogen atom are joined to the 6- and 8-positions of the nucleus, so that the $-N[-(CH_2)_3-]_2$ grouping and the benzene ring of the nucleus together form a julolidine ring system.

43. A process for the preparation of a squarylium compound of the formula:



wherein Q^1 is an aromatic heterocyclic nucleus such that in the compound of formula $Q^1CH_2R^1$ the methylene hydrogens are active hydrogens, R^1 is a hydrogen atom or an aliphatic or cycloaliphatic group, and Q^3 is an aromatic nucleus bearing an electron-donating group,

which process comprises reacting a squaric acid derivative of the formula:



wherein Q^1 and R^1 are as defined above, with a compound of the formula Q^3H.

44. A process according to claim 43 wherein the compound of the formula Q^3H is an N,N-disubstituted aniline.